

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C23C 22/38	A1	(11) International Publication Number: WO 91/13186 (43) International Publication Date: 5 September 1991 (05.09.91)
(21) International Application Number: PCT/US91/00965 (22) International Filing Date: 13 February 1991 (13.02.91) (30) Priority data: 2/40168 21 February 1990 (21.02.90) JP 2/40169 21 February 1990 (21.02.90) JP (71) Applicant (for all designated States except US): HENKEL CORPORATION [US/US]; 300 Brookside Avenue, Ambler, PA 19002 (US). (72) Inventors; and (75) Inventors/Applicants (for US only) : YOSHIDA, Masayuki [JP/JP]; Nihon Parkerizing Kibogaoka Dormitory, No. 5, 20-4, Nakao-cho, Asahi-ku, Yokohama-shi, Kanagawa-ken (JP). NAKADA, Kazuya [JP/JP]; Nihon Parkerizing Hiratsuka Dormitory, 2566, Shinomiya, Hiratsuka-shi, Kanagawa-ken (JP).		(74) Agent: WISDOM, Norvell, E., Jr.; Henkel Corporation, Law Department, 140 Germantown Pike, Suite 150, Plymouth Meeting, PA 19462 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CONVERSION TREATMENT METHOD AND COMPOSITION FOR ALUMINUM AND ALUMINUM ALLOYS (57) Abstract The paint adhesion and corrosion resistance of surfaces of aluminum and its alloys, particularly when using a paint based on poly(vinyl chloride), is improved by using a conversion coating solution having a pH in the range from 1.0 to 3.0 and containing: (A) an amount of phosphate ions that is stoichiometrically equivalent to at least 5.0 g/L of phosphoric acid; (B) at least 1.0 g/L of hexavalent chromium; (C) at least 0.1 g/L of fluoride ions; and (D) a complex fluoride ion component selected from the group consisting of: (i) at least 4.0 g/L of fluosilicate ions, (ii) at least 0.5 g/L of fluoborate ions, (iii) at least 2.0 g/L of fluozirconate ions, and (iv) at least 2.0 g/L of fluotitanate ions.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

**CONVERSION TREATMENT METHOD AND COMPOSITION FOR ALUMINUM
AND ALUMINUM ALLOYS**

TECHNICAL FIELD

The present invention relates to a novel conversion treatment solution for aluminum and aluminum alloys which imparts an excellent corrosion resistance and paint adherence to the surface of aluminum and aluminum alloys prior to their being painted and to a process of treating surfaces with such a solution. The conversion treatment solution is particularly well suited for application to the surface of, for example, the lid material for beverage cans (i.e., can end stock) and the like.

BACKGROUND ART

Conversion treatment solutions for aluminum and aluminum alloys may be roughly classified into chromate-type treatments and nonchromate-type treatments. Typical examples of chromate-type treatments are chromic acid/chromate treatments and phosphoric acid/chromate treatments. Chromic acid/chromate treatments came into practical application in about 1950, and are still widely used at present on, for example, the fin material of heat exchangers. The principal components of this type of conversion treatment solution are chromic acid (CrO_3) and hydrofluoric acid (HF), and an accelerator may also be present. A film which contains some quantity of hexavalent chromium is formed.

The phosphoric acid/chromate conversion treatment is disclosed in United States Patent Number 2,438,877. This conversion treatment solution is composed of chromic acid (CrO_3), phosphoric acid (H_3PO_4), and hydrofluoric acid (HF). The principal component of the resulting film is hydrated chromium phosphate ($\text{CrPO}_4 \cdot 4\text{H}_2\text{O}$). Since this film does not contain much if any hexavalent chromium, it is widely used at present as a paint undercoating treatment for beverage cans and the associated lid stock.

Nonchromate-type treatments are recognized in the art as a distinct category from the chromate-type treatment solutions explained above, and are exemplified by the inven-

tion disclosed in Japanese Patent Application Laid Open [Kokai] Number 52-131937 [131,937/77]. The treatment solution disclosed therein comprises an acidic (pH approximately 1.0 to 4.0) aqueous coating solution which contains zirconium or titanium or a mixture thereof as well as phosphate and fluoride. Treatment with the disclosed conversion treatment solution produces on the aluminum surface a conversion film whose main component is zirconium and/or titanium oxide. Although the absence of hexavalent chromium is an advantage of the nonchromate-type treatment solution, this type of treatment solution nevertheless suffers from a corrosion resistance and paint adherence inferior to those for chromate-type treatments.

Aluminum alloy, in sheet or coil form, is widely used after painting for beverage can lid material, i.e., can end stock. It is subjected to a conversion treatment in order to raise the corrosion resistance and paint adherence, and the phosphoric acid/chromate treatment is employed in almost all commercial can lid manufacturing in Japan.

The phosphoric acid/chromate conversion treatment of can end stock generally employs a treatment solution which contains 10.0 to 40.0 g/L phosphate ion, 2.0 to 4.0 g/L hexavalent chromium, and 0.7 to 1.5 g/L fluoride ion. At present, vinyl chloride paint is generally used to coat can end stock. Thus, the production of can ends normally includes a phosphoric acid/chromate treatment of aluminum alloy in coil or sheet form, followed by coating with a vinyl chloride paint and then forming.

A beverage can thus normally consists of a can end formed from aluminum alloy coil or sheet treated as described above and of a can body filled with, for example, juice or beer. Depending on its contents, the can may be subjected to sterilization at relatively high temperatures after filling. If it is, steam is formed from vaporization of the contents, the steam penetrates through the paint film, and the permeated steam then condenses at the interface between the paint film and conversion film. As

a result, sterilization tends to reduce the adherence of the paint film. In particular, when a section of the can end is opened by the easy-open method, defects (enamel feathering) can be generated in the opened region due to peeling or exfoliation of the paint film.

DESCRIPTION OF THE INVENTION

Problem to Be Solved by the Invention

Increasing the adhesion of paint to aluminum and its alloys, particularly aluminum and its alloys used in forming beverage can ends to be used for cans requiring high temperature sterilization of the contents, is the major problem addressed by this invention.

Summary of the Invention

As a concrete means for solving the problems described hereinbefore for the prior art, the present invention introduces an aqueous conversion treatment solution for aluminum and aluminum alloys which is characterized in that its pH is in the range from 1.0 to 3.0 and in that it comprises, or preferably consists essentially of, water and 5.0 to 40.0 grams per liter ("g/L") of phosphate ions, 1.0 to 4.0 g/L of hexavalent chromium (in the form of chromium containing anions), 0.1 to 2.0 g/L of fluoride ions, and a complex fluoride ion component selected from the group consisting of (i) 4.0 to 15.0 g/L of fluosilicate ion, (ii) 0.5 to 3.0 g/L of fluoborate ion, (iii) 2.0 to 8.0 g/L of fluozirconate ions, and (iv) 2.0 to 8.0 g/L of fluotitanate ions. This conversion treatment solution is capable of forming a highly paint-adherent conversion film which imparts an excellent corrosion resistance to the surface of aluminum and aluminum alloys. In other words, the present invention seeks to offer a conversion treatment solution which imparts an excellent corrosion resistance and paint adherence to the surface of aluminum and aluminum alloy prior to their being painted.

Details of Preferred Embodiments of the Invention

Th conversion treatment solution of the present invention is an acidic treatment solution which contains

complex fluoride ion, phosphat ion, hexavalent chromium, and fluoride ion as its essential components.

The complex fluoride ions are selected from fluosilicate (SiF_6^{-2}) ions, fluotitanate (TiF_6^{-2}), fluozirconate (ZrF_6^{-2}), and fluoborate (BF_4^{-2}) ions, and may be added in the form of fluosilicic acid, fluoboric acid, fluozirconic acid, fluotitanic acid, or any soluble salt thereof. Mixtures of these ions may also be used. A range of 4.0 to 15.0 g/L is preferred for the fluosilicate ion. Values less than 4.0 g/L cannot normally generate good paint adherence, while values exceeding 15.0 g/L may cause substantial etching of an aluminum surface and prevent the formation of a satisfactory film. A range of 0.5 to 3.0 g/L is preferred for the fluoborate ion. Values less than 0.5 g/L again cannot usually generate a good paint adherence, while values in excess of 3.0 g/L increase waste water pollution and are uneconomical. A range of 2.0 to 8.0 g/L is preferred for fluozirconate ions, fluotitanate ions, or mixtures of these two ions. Concentrations of these two complex fluoride ions that are less than 2.0 g/L cannot usually generate good paint adherence, while concentrations exceeding 8.0 g/L cause substantial etching and usually prevent the formation of a satisfactory film.

Phosphoric acid (H_3PO_4) is the preferred source for the phosphate ion, and the preferred phosphoric acid content falls into the range of 5.0 to 40.0 g/L. When this value is less than 5.0 g/L, the resulting film will normally contain only small quantities of chromium phosphate and the paint adherence may be inadequate. While good films are formed at concentrations exceeding 40.0 g/L, the cost of the treatment solution is also increased and the economics become less favorable.

Chromic acid (CrO_3) is the preferred source for the hexavalent chromium, and the preferred chromic acid content is that which will result in a concentration of its stoichiometric equivalent as hexavalent chromium in the range from 1.0 to 4.0 g/L. Values less than 1 g/L result in an

inferior corrosion resistance because a satisfactory conversion film is not formed. Values in excess of 4.0 g/L can cause increased pollution from and/or pollution abatement cost for waste water from the treatment solution and thus create environmental and economic problems.

The fluoride ion content is an important component for controlling the film growth rate of the conversion film. The fluoride ion source may be, for example, hydrofluoric acid (HF), sodium fluoride (NaF), potassium fluoride (KF), and the like. The fluoride ion concentration in the conversion solutions was determined as follows: An ion-selective electrode (Fluorine F-125 electrode, reference HS-305DP from Toa Denpa Kogyo Kabushiki Kaisha) and an ion meter (Type IM-40S from Toa Denpa Kogyo Kabushiki Kaisha) were used. For calibration, standard solutions were prepared by adding a specified quantity of hydrofluoric acid (for example, 0.1 g/L, 1 g/L, or 10 g/L) to 5 g/L chromic acid and 15 g/L phosphoric acid and by adjusting the pH to 2.0 with phosphoric acid or sodium hydroxide. (The fluoride ion concentration was assumed to correspond to the total quantity of fluorine from hydrofluoric acid addition). The meter readings obtained with these solutions of known fluoride ion concentration were then determined and plotted against the fluoride ion concentrations to generate a calibration curve. The pH of the conversion solution itself was adjusted to 2.0 using phosphoric acid or sodium hydroxide and then measured using the fluorine ion meter, and the measured value was converted to the fluoride ion concentration by reference to the calibration curve.

The preferred range for the fluoride ion concentration is 0.1 to 2.0 g/L. At values less than 0.1 g/L, the growth rate of the conversion film is slow, so that long treatment times must be used in order to obtain satisfactory conversion films and the productivity is therefore low. Rapid growth rates are encountered at values in excess of 2.0 g/L; this results in large film weights and an undesirable loss of the metallic luster of the workpiece. As a conse-

quence, the preferred concentration range is 0.1 to 2.0 g/L; the particularly preferred range is 0.4 to 1.0 g/L.

5 The pH of this conversion treatment solution should be in the range of 1.0 to 3.0 and may conveniently be adjusted into that range through the use of an acid arbitrarily selected from acids such as phosphoric acid, nitric acid, and hydrochloric acid or a base arbitrarily selected from bases such as sodium hydroxide, ammonium hydroxide, and the like. A pH below 1.0 causes substantial etching and therefore interferes with coat formation. A pH in excess of 3.0 usually results in weak etching so that a uniform film cannot be formed.

15 The use of the conversion treatment solution of the present invention in treatment processes is another embodiment of this invention and will now be considered in more detail. The conversion treatment solution of the present invention can be used as a substitute for the currently widely used phosphoric acid/chromate treatment solutions. A preliminary surface cleaning must usually be carried out when the conversion treatment solution of the present invention is used for the conversion treatment of the surface of aluminum or aluminum alloy. The cleaning method in this case may consist of treatment with an acidic, alkaline, or solvent-based cleaning solution or some combination thereof. As necessary or desired, the aluminum or aluminum alloy surface may be etched with alkali or acid after cleaning. Either immersion or spray treatment may be used as the method for treatment with solution according to the present invention. The weight of the resulting conversion film is governed by such factors as the treatment temperature and treatment time. The temperature of the treatment solution should preferably fall into the range from room temperature (about 20 degrees Centigrade) to 70 degrees Centigrade and more preferably falls into the range from 35 to 55 degrees Centigrade. Treatment times in the range of 1 to 90 seconds are preferred. As with phosphoric acid/chromate films, the conversion film weight is normally

evaluated based on the deposition of chromium, zirconium, and/or titanium. The quantity of deposition of each of the three metals, when present at all, preferably falls within the range of 5 to 50 mg/m², and should be adjusted in accordance with the required degree of corrosion resistance. The deposition of chromium, titanium, and/or zirconium can be controlled by suitably adjusting the treatment temperature and treatment time.

The conversion film formed by the conversion treatment solution according to the present invention when neither zirconium or titanium is present is believed to be chemically and physically similar to the film formed by phosphoric acid/chromate treatments, and is composed principally of hydrated chromium phosphate (CrPO₄·4H₂O). When either fluotitanate or fluozirconate is included in the treatment solution, the conversion film usually contains both hydrated chromium phosphate and zirconium oxide (ZrO₂) and/or titanium oxide (TiO₂).

20

Examples

The conversion treatment solution of the present invention is explained in greater detail below through the use of several illustrative examples. The first group of examples are for solutions containing fluoborate or fluosilicate ions, and the effectiveness of such solutions relative to comparison examples is reported in Table 1.

The substrate for these examples was an aluminum/magnesium alloy (described in detail in Japanese Industrial Standard (hereinafter "JIS") A5082). This aluminum alloy was degreased and conversion treated using a small sprayer designed to give spraying conditions identical to those currently encountered in typical spray treatments on commercial continuous conversion treatment lines for the conversion treatment of aluminum alloy coil. Chromium content in the coating deposited by the conversion process was measured using a fluorescent X-ray analyzer (Model 3070E from

Table 1: RESULTS OF EVALUATION TESTING

		Conversion Film Areal Density in <u>mg of Cr/m²</u>	Salt Spray Test Time, <u>Hours</u>	Peel Test Strength, <u>Kg/5 mm</u>	Alcoa Test Residual <u>Width, mm</u>
5					
10	Example 1	20	2500	3.6	0.2
	Example 2	20	2500	3.2	0.3
	Example 3	15	2300	3.5	0.3
	Example 4	25	2800	3.6	0.2
	Example 5	20	2500	3.2	0.3
15	Example 6	20	2500	3.2	0.3
	Example 7	20	2500	3.4	0.2
	Example 8	30	3000	3.4	0.2

20	Comparison Example 1	20	2500	2.5	0.6
	Comparison Example 2	15	2000	2.5	0.7
	Comparison Example 3	20	2500	2.0	0.8
25	Comparison Example 4	20*	1700	1.3	1.0

* This figure is the areal density of Zr rather than Cr.

30 Rigaku Denki Kogyo). This conversion treated aluminum alloy sheet was then coated with a can end paint of a poly (vinyl chloride) type to give a paint film thickness of 12 to 14 micrometers, which was then baked at 200 degrees Centigrade for 10 minutes before the sheets were subjected to the other tests reported in Table 1.

35 Salt-spray testing was conducted in order to evaluate the corrosion resistance. Salt-spray testing was conducted in accordance with JIS Z-2371, and the value reported is the time required for the appearance of blistering at a cross form cut in the paint film on the painted test panel.

40 Thus, longer times correspond to a better corrosion resist-

ance. Spray times of 2000 hours or more are generally now rated as excellent.

5 The paint adherence was evaluated as follows The painted test sheet was cut into 5 x 150 millimeter (hereinafter "mm") size rectangular strips, which were then hot-press-bonded with polyamide film. The obtained test specimen was immersed in boiling deionized water for 3 hours, and the peel strength was then evaluated in a 180° peel test. High peel strength values correspond to a better paint adherence, and as a general rule a value of 3.0 kilograms of force (hereinafter "kgf") per 5 mm width is rated as excellent.

10 Enamel feathering was evaluated in accordance with the Alcoa method, as described on page 49 of the Lecture Notes from the 73rd Fall Meeting of Keikinzoku Gakkai [Institute of Light Metals of Japan]. This evaluation is based on the maximum residual paint film width after peeling. Thus, smaller residual paint film widths correspond to a more desirable smaller amount of enamel feathering, and as a general rule residual widths not exceeding 0.5 mm are rated as excellent.

Example 1

25 The surface of the aluminum alloy was cleaned by rinsing with a hot (70 degrees Centigrade) 4 % aqueous solution of a commercial strongly alkaline degreaser (FINE CLEANER™ 4418 from Nihon Parkerizing Company, Limited) and then with water. This was followed by spraying for 5 seconds with conversion treatment solution 1 heated to 50 degrees Centigrade, rinsing again with tap water, spraying with deionized water (specific resistance $\geq 3,000,000$ ohm-cm) for 10 seconds, and finally drying in a hot-air drying oven at 70 degrees Centigrade for 5 minutes. After drying, the conversion coated test panel was painted as described above, and the corrosion resistance, paint adherence, and enamel feathering were then evaluated.

35 Conversion treatment solution 1 contained 18.8 g/L of 40% fluosilicic acid (H_2SiF_6) = 7.4 g/L of SiF_6^{2-} ; 21.3 g/L of

75 % phosphoric acid (H_3PO_4) = 15.5 g/L of PO_4^{3-} ; 5.8 g/L of chromic acid (CrO_3) = 3.0 g/L of Cr^{6+} ; and 3.0 g/L of 20 % hydrofluoric acid (HF) = 0.6 g/L of F^- ; the pH was adjusted to 2.0 with ammonium hydroxide after all the other ingredients had been added.

Example 2

This was identical to Example 1, except that the Conversion treatment solution 2 used contained only 12.5 g/L of 40 % fluosilicic acid = 4.9 g/L of SiF_6^{2-} , rather than the larger amount in Conversion treatment solution 1.

Example 3

This was identical to Example 2, except that (i) the Conversion treatment solution 3 used contained only 2.9 g/L of chromic acid = 1.5 g/L of Cr^{6+} , rather than the larger amount in Conversion treatment solution 2 and (ii) the pH was adjusted to 1.5 with hydrochloric acid rather than to 2.0 with ammonium hydroxide as in Conversion treatment solution 2.

Example 4

This was identical to Example 1, except that the Conversion treatment solution 4 used contained 5.0 g/L of 20 % hydrofluoric acid = 1.0 g/L of F^- , rather than the smaller amount in Conversion treatment solution 1.

Example 5

This was identical to Example 1, except that the Conversion treatment solution 5 used contained 1.0 g/L of sodium fluoborate (NaBF_4) = 0.8 g/L of BF_4^- , instead of the fluosilicic acid used in Conversion treatment solution 1.

Example 6

This was identical to Example 5, except that (i) the Conversion treatment solution 6 used contained 2.0 g/L of sodium fluoborate (NaBF_4) = 1.6 g/L of BF_4^- , rather than the smaller amount in Conversion treatment solution 5 and (ii) the pH was adjusted to 2.5 instead of 2.0.

Example 7

This was identical to Example 1, except that the samples were spray treated for 10 seconds at 40 degrees Centi-

grade rather than for 5 seconds at 50 degrees Centigrade as in Example 1.

Example 8

5 This was identical to Example 1, except that the samples were spray treated for 10 seconds rather than for 5 seconds as in Example 1.

Comparison Example 1

10 This was identical to Example 1, except that the Conversion treatment solution 7 used contained only 6.3 g/L of 40 % fluosilicic acid = 2.5 g/L of SiF_6^{2-} , rather than the larger amount in Conversion treatment solution 1.

Comparison Example 2

15 This was identical to Example 1, except that the Conversion treatment solution 8 used contained 40.0 g/L of 40 % fluosilicic acid = 15.8 g/L of SiF_6^{2-} , rather than the smaller amount in Conversion treatment solution 1.

Comparison Example 3

20 The aluminum alloy was cleaned as in Example 1 and then spray-treated for 5 seconds with a 5 % aqueous solution of a commercial phosphoric acid/chromate treatment concentrate (ALCHROM™ K702 from Nihon Parkerizing Company, Limited) heated to 50 degrees Centigrade. After this treatment, it was rinsed with water, dried, and painted as in Example 1, and its performance was then evaluated.

25 Comparison Example 4

30 The aluminum alloy was cleaned as in Example 1 and then spray-treated for 30 seconds with a 2 % aqueous solution of a commercial non-chromate treatment concentrate (PARCOAT™ K3761 from Nihon Parkerizing Company, Limited) heated to 50 degrees Centigrade. After this treatment, it was rinsed with water, dried, and painted as in Example 1, and its performance was then evaluated.

35 Another group of examples and comparison examples utilized solutions containing fluozirconate or fluotitanate ions, as described in more detail below.

Example 9

This was identical to Example 1, except that the Con-

version Solution 9 used contained 20.2 g/L of 20 % aqueous fluozirconic acid (H_2ZrF_6) = 4.0 g/L of ZrF_6^{-2} instead of the fluosilicic acid used in Conversion Solution 1 in Example 1.

5 Example 10

This was identical to Example 9, except that the Conversion Solution 10 used contained 12.6 g/L of 20 % aqueous fluozirconic acid (H_2ZrF_6) = 2.5 g/L of ZrF_6^{-2} instead of the larger amount of fluozirconic acid used in Conversion Solution 9 in Example 9.

10 Example 11

This was identical to Example 9, except that the Conversion Solution 11 used (i) contained 1.9 g/L of chromic acid = 1.0 g/L of Cr^{+6} instead of the larger amount of chromic acid in Conversion Solution 1 in Example 1 and (ii) had a pH of 1.5 achieved by adjustment with hydrochloric acid rather than a pH of 2.0 achieved by adjustment with ammonia as in Conversion Solution 9.

15 Example 12

This was identical to Example 11, except that the Conversion Solution 11 used contained 5.8 g/L of chromic acid = 3.0 g/L of Cr^{+6} and 5.0 g/L of 20 % aqueous hydrofluoric acid = 1.0 g/L of F^- ions instead of the smaller amounts of these two constituents used in Conversion Solution 11 in Example 11.

20 Example 13

This was identical to Example 9, except that the Conversion Solution 13 used (i) contained 20.3 g/L of aqueous fluotitanic acid = 4.0 g/L of TiF_6^{-2} instead of the fluozirconic acid in Conversion Solution 9 in Example 9 and (ii) had a pH of 2.5 achieved by adjustment with sodium hydroxide rather than a pH of 2.0 achieved by adjustment with ammonia as in Conversion Solution 9.

25 Example 14

This was identical to Example 9, except that the Conversion Solution 14 used contained 12.7 g/L of 20 % aqueous fluotitanic acid = 1.6 g/L of TiF_6^{-2} and 12.6 g/L of 20 %

aqueous fluozirconic acid = 2.5 g/L of ZrF_6^- ions instead of the larger amount of fluozirconic acid, with no fluotitanic acid, used in Conversion Solution 9 in Example 9.

Example 15

- 5 This was identical to Example 9, except that the samples were spray treated for 10 seconds at 40 degrees Centigrade rather than for 5 seconds at 50 degrees Centigrade as in Example 9.

Example 16

- 10 This was identical to Example 9, except that the samples were spray treated for 10 seconds rather than for 5 seconds as in Example 9.

Comparison Example 5

- 15 This was identical to Example 9, except that the Conversion treatment solution 15 used contained only 5.0 g/L of 20 % fluozirconic acid = 1.0 g/L of ZrF_6^{2-} , rather than the larger amount in Conversion treatment solution 9.

Comparison Example 6

- 20 This was identical to Example 9, except that the Conversion treatment solution 16 used contained 50.0 g/L of 20 % fluozirconic acid = 15.8 g/L of ZrF_6^{2-} , rather than the smaller amount of fluozirconic acid in Conversion treatment solution 9.

- 25 Test results from this second group of examples are shown in Table 2, where Comparison Examples 3 and 4 are repeated from Table 1.

Benefit of the Invention

- 30 As Tables 1 and 2 make clear, application of the conversion treatment solution of the present invention affords an excellent corrosion resistance and paint adherence as well as an excellent resistance enamel feathering.

Table 2: RESULTS OF TESTING WITH FLUOZIRCONATE AND
FLUOTITANATE CONTAINING SOLUTIONS

5		Areal Density in Conversion			Salt Spray Test Time, Hours	Peel Test Strength, Kg Force/ 5 mm width	Alcoa Test Residual Width, mm
		Film of:					
		Cr	Zr	Ti			
10	Example 9	20	20	—	2500	3.8	0.2
	Example 10	20	15	—	2500	3.3	0.3
	Example 11	15	20	—	2500	3.4	0.3
	Example 12	25	25	—	2800	3.5	0.2
	Example 13	20	—	20	2500	3.3	0.3
15	Example 14	20	15	15	2800	3.2	0.3
	Example 15	20	20	—	2500	3.5	0.2
	Example 16	30	30	—	3000	3.5	0.2

20	Comparison Example 5	20	10	—	2500	2.5	0.6
	Comparison Example 6	15	15	—	2000	2.5	0.7
	Comparison Example 3	20	—	—	2500	2.0	0.8
25	Comparison Example 4	—	20	—	1700	1.3	1.0

CLAIMS

1. An aqueous conversion coating solution characterized in that it has a pH value from 1.0 to 3.0 and comprises:
 - (A) an amount of phosphate ions that is stoichiometrically equivalent to at least 5.0 g/L of phosphoric acid;
 - (B) at least 1.0 g/L of hexavalent chromium;
 - (C) at least 0.1 g/L of fluoride ions; and
 - (D) a complex fluoride ion component selected from the group consisting of:
 - (i) at least 4.0 g/L of fluosilicate ions,
 - (ii) at least 0.5 g/L of fluoborate ions,
 - (iii) at least 2.0 g/L of fluozirconate ions, and
 - (iv) at least 2.0 g/L of fluotitanate ions.
2. An aqueous solution according to claim 1, characterized in that it comprises:
 - (A) an amount of phosphate ions that is stoichiometrically equivalent to from 5.0 to 40.0 g/L of phosphoric acid;
 - (B) from 1.0 to 4.0 g/L of hexavalent chromium;
 - (C) from 0.1 to 2.0 g/L of fluoride ions; and
 - (D) a complex fluoride ion component selected from the group consisting of:
 - (i) from 4.0 to 15.0 g/L of fluosilicate ions,
 - (ii) from 0.5 to 3.0 g/L of fluoborate ions,
 - (iii) from 2.0 to 8.0 g/L of fluozirconate ions, and
 - (iv) from 2.0 to 8.0 g/L of fluotitanate ions.
3. An aqueous solution according to claim 2, characterized in that it comprises from 0.4 to 1.0 g/L of fluoride ions.
4. An aqueous solution according to claim 1, characterized in that it comprises from 0.4 to 1.0 g/L of fluoride ions.
5. A process for treating a surface of aluminum or an aluminum alloy, said process comprising steps of forming a conversion coating on said surface and subsequently overcoating the conversion coated surface with an organic pro-

protective coating, characterized in that the improvement comprises forming the conversion coating on said surface by contacting said surface with an aqueous solution having a pH value from 1.0 to 3.0 and comprising:

- 5 (A) an amount of phosphate ions that is stoichiometrically equivalent to at least 5.0 g/L of phosphoric acid;
 - (B) at least 1.0 of hexavalent chromium;
 - (C) at least 0.1 g/L of fluoride ions; and
 - 10 (D) a complex fluoride ion component selected from the group consisting of:
 - (i) at least 4.0 g/L of fluosilicate ions,
 - (ii) at least 0.5 g/L of fluoborate ions,
 - (iii) at least 2.0 g/L of fluozirconate ions, and
 - (iv) at least 2.0 g/L of fluotitanate ions.
- 15 6. A process according to claim 5, characterized in that said aqueous solution comprises:
- (A) an amount of phosphate ions that is stoichiometrically equivalent to from 5.0 to 40.0 g/L of phosphoric acid;
 - (B) from 1.0 to 4.0 g/L of hexavalent chromium;
 - 20 (C) from 0.1 to 2.0 g/L of fluoride ions; and
 - (D) a complex fluoride ion component selected from the group consisting of:
 - (i) from 4.0 to 15.0 g/L of fluosilicate ions,
 - (ii) from 0.5 to 3.0 g/L of fluoborate ions,
 - 25 (iii) from 2.0 to 8.0 g/L of fluozirconate ions, and
 - (iv) from 2.0 to 8.0 g/L of fluotitanate ions.
7. A process according to claim 6, characterized in that said aqueous solution comprises from 0.4 to 1.0 g/L of fluoride ions.
- 30 8. A process according to claim 5, characterized in that said aqueous solution comprises from 0.4 to 1.0 g/L of fluoride ions.
9. A process according to claim 8, characterized in that the conversion coating formed contains from 5 to 50 milligrams per square meter of at least one of chromium, zirconium, or titanium.
- 35


10. A process according to claim 7, characterized in that the conversion coating formed contains from 5 to 50 milligrams per square meter of at least one of chromium, zirconium, or titanium.
- 5 11. A process according to claim 6, characterized in that the conversion coating formed contains from 5 to 50 milligrams per square meter of at least one of chromium, zirconium, or titanium.
- 10 12. A process according to claim 5, characterized in that the conversion coating formed contains from 5 to 50 milligrams per square meter of at least one of chromium, zirconium, or titanium.
- 15 13. A process according to claim 12, characterized in that the conversion coating is performed at a temperature in the range from 20 to 70 degrees Centigrade.
14. A process according to claim 11, characterized in that the conversion coating is performed at a temperature in the range from 20 to 70 degrees Centigrade.
- 20 15. A process according to claim 10, characterized in that the conversion coating is performed at a temperature in the range from 20 to 70 degrees Centigrade.
16. A process according to claim 9, characterized in that the conversion coating is performed at a temperature in the range from 20 to 70 degrees Centigrade.
- 25 17. A process according to claim 16, characterized in that the conversion coating is performed at a temperature in the range from 35 to 55 degrees Centigrade for a contact time in the range from 1 to 90 seconds.
- 30 18. A process according to claim 15, characterized in that the conversion coating is performed at a temperature in the range from 35 to 55 degrees Centigrade for a contact time in the range from 1 to 90 seconds.
19. A process according to claim 14, characterized in that the conversion coating is performed at a temperature in the

range from 35 to 55 degrees Centigrade for a contact time in the range from 1 to 90 seconds.

20. A process according to claim 13, wherein the conversion coating is performed at a temperature in the range from 35 to 55 degrees Centigrade for a contact time in the range from 1 to 90 seconds.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/00965

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 23 C 22/38		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 23 C	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁶	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 2868682 (GAILLARD W. DELL) 13 January 1959 see claim 1; examples page 7 ---	1
Y	EP, A, 0348890 (NKK CORP.) 3 January 1990 see claim 1; table 1-e; examples 61-65; page 16; page 7, lines 45-49 ---	1-20
Y	US, A, 3377212 (NELSON J. NEWHARD) 9 April 1968 see claim 1; column 4, lines 13-21; example 8 ---	1-20
A	FR, A, 2198001 (SOCIETE CONTINENTALE PARKER) 29 March 1974 ---	
A	FR, A, 2268875 (ALLMANNA SVENSKA ELEKTRISKA AKTIEBOLAGET) 21 November 1975 ---	
A	Chemical Abstracts, volume 98, no. 16, 1983, see page 284, abstract 130913j & CS 198862 (KRIZKOVA) 1 August 1978 -----	
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
7th June 1991	01.08.91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	F.W. HECK 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9100965

SA 44941

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16/07/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 2868682		BE-A- 563956 CH-A- 373616 DE-B- 1096153 FR-A- 1190562 GB-A- 830632 NL-C- 107091 NL-A- 224487	
EP-A- 0348890	03-01-90	JP-A- 2015177 AU-A- 3678889 US-A- 4971636	18-01-90 04-01-90 20-11-90
US-A- 3377212		DE-A- 1621423 FR-A- 1544482 GB-A- 1153668	17-12-70 29-05-69
FR-A- 2198001	29-03-74	BE-A- 800404 DE-A- 2242908 GB-A- 1376120 SE-B- 385131	01-10-73 14-03-74 04-12-74 08-06-76
FR-A- 2268875	21-11-75	SE-B- 396024 DE-A- 2516611 JP-A- 50149570 SE-A- 7405605	05-09-77 13-11-75 29-11-75 27-10-75